

Contents

Part I The Activity in Classical Thermodynamics

1	Thermodynamic Systems	3
1.1	Thermodynamic Systems	3
1.2	State of a System	4
1.3	Extensive and Intensive Properties	5
1.4	Transformation	5
1.5	Thermodynamic Equilibrium	5
1.6	State Functions	5
1.7	Reversible or Quasi-Static Processes and Irreversible Processes	6
1.8	Different Expressions of the Composition of a Solution	6
2	Gibbs and Helmholtz Energies	11
2.1	Brief Recalls About the Second Principle and Entropy	12
2.1.1	General Points	12
2.1.2	Studied System, Surroundings, and Isolated System	13
2.2	Gibbs Energy	13
2.3	Some Properties of the Gibbs Energy Function	15
2.3.1	Changes in the Gibbs Energy with the Pressure and the Temperature	15
2.3.2	Gibbs–Helmholtz Equation	16
2.4	Helmholtz Energy	17
2.5	Gibbs and Helmholtz Energies, Potential Functions: Thermodynamic Potentials	18
2.5.1	Potential Energy and Evolution of a Mechanical System	18
2.5.2	Entropy and Thermodynamic Potential	19
2.5.3	Generalization: Definition of a Thermodynamic Potential	19

3	Escaping Tendency	21
3.1	Analogy of the Equilibrium Distribution of the Matter with the Thermal One Between Two Bodies	22
3.2	The Molal Gibbs Energy of a Substance as a Measure of Its Escaping Tendency	22
3.3	Change of Molal Gibbs Energy of a Perfect Gas with Pressure	23
3.4	Gibbs Energy Change Accompanying a Reaction Between Perfect Gases	25
4	Partial Molar Quantities	27
4.1	Closed and Open Systems	27
4.2	On the Necessity to Introduce the Partial Molar Quantities When the Species Are in Solution	28
4.3	Definition of Partial Molar Quantities	30
4.4	Physical Meaning of the Partial Molal Quantities	31
4.5	Molal Quantities and Partial Molal Quantities	32
4.6	Fundamental Equation of the Molal Partial Quantities	33
4.7	Thermodynamic Relations Between Partial Molar Quantities	34
4.8	Experimental Determination of Partial Molal Quantities	34
5	Chemical Potential or Partial Molal Gibbs Energy	35
5.1	Definitions of the Chemical Potential	35
5.2	Physical Meaning of the Chemical Potential: Equilibrium Condition	37
5.3	Some Properties of the Chemical Potential	38
5.4	Change in the Gibbs Energy Accompanying a Chemical Transformation	41
5.5	Electromotive Force of a Reversible Electrochemical Cell and Change in the Gibbs Energy Accompanying the Reaction Cell	42
6	The Notion of Activity: An Overview	43
6.1	Some Properties of the Quantity Activity: Activities and Chemical Equilibria	43
6.2	Activities and Concentrations	44
6.3	Chemical Potential and Activity of a Compound	45
6.4	Standard State and Activity	45
6.5	On the Arbitrary Character of the Choice of the Standard State	46
6.6	Activity and Fugacity	46
6.7	Ideal Character of a System and Interactions Between the Particles Constituting It	47
6.8	Intermolecular Forces	48
6.9	Determination of Activities	48
6.10	Genesis of the Chemical Activity Concept	49

7	The Fugacity Quantity	51
7.1	Definition of the Fugacity of a Pure Gas	52
7.2	Chemical Potential of a Perfect or Real Pure Gas in Terms of Fugacities	55
7.3	Fugacity of Liquids and Solids	56
7.4	Fugacity Coefficient of a Real Gas	56
7.5	Coming Back to the Reference State	57
7.6	Changes in Fugacity with the Temperature and the Pressure .	57
7.7	Physical Significance of the Fugacity	59
7.8	Expressions of the Chemical Potential of a Component of a Mixture of Perfect Gases	59
7.9	Fugacities and Mixtures of Real Gases	61
7.9.1	Expressions of the Chemical Potential of the Components	61
7.9.2	Change of the Fugacity of One Component of a Gaseous Mixture with the Pressure	62
7.9.3	Change in the Fugacity of a Component of a Mixture of Real Gases with the Temperature . .	63
7.10	Determination of the Fugacity of a Gas in a Gaseous Mixture	63
7.11	Fugacity and Heterogeneous Equilibria	64
7.12	Other Use of the Fugacities	65
7.13	Fugacity and the Gibbs–Duhem Relation	65
8	Ideal Solutions	67
8.1	Definition of Ideal Solutions	68
8.2	Ideal, Perfect, and Sufficiently Diluted Solutions	69
8.3	Raoult's Law	69
8.3.1	Raoult's Law (Strictly Speaking)	69
8.3.2	Equivalence of the Definition of Perfect Solutions and the Fact That the Solution Obeys Raoult's Law	70
8.4	Behavior of the Second Component of a Binary Liquid Mixture When the First One Obeys Relation (8.7) in the Whole Range of Concentrations	71
8.5	Diluted Solutions: Henry's Law	73
8.5.1	Henry's Law	73
8.5.2	Henry's Law and Other Expressions of the Composition of the Solution	74
8.6	About the Differences Between Henry's and Raoult's Laws	75
8.7	Fundamental Interest of Raoult and Henry's Laws	75
8.8	Consequences of the Ideal Character: Partial Molal Enthalpies and Partial Molal Volumes of the Components of an Ideal Solution	76
8.9	Colligative Properties	76

8.10	The Osmotic Pressure	77
8.11	Nonideal Solutions	80
8.11.1	Margules' Relations	80
8.11.2	Van Laar Relations	81
9	Definitions of an Activity	83
9.1	Definitions of the Activity	84
9.1.1	Starting from the Notion of Fugacity	84
9.1.2	Starting from the Notion of the Chemical Potential	84
9.1.3	Consequence of the Arbitrary Character of the Standard State	86
9.1.4	Definition of the Standard Chemical Potential of a Species	86
9.2	The Activity Coefficient	86
9.3	A First Sight of the Physical Significance of the Quantities Activity and Activity Coefficient	87
9.4	A First Return to the Standard State	88
9.5	Consequences of the Arbitrary Character of the Standard State	89
9.6	Some Properties of the Activity Function	90
9.6.1	Dependence of the Activity on the Pressure	90
9.6.2	Dependence of the Activity on the Temperature	91
10	Activities of Gases	93
10.1	Usual Standard State and Activity of a Pure Gas	93
10.2	Usual Standard State and Activity of a Gas in a Gaseous Mixture	96
10.3	Reference State and Standard State	98
10.4	General Expression of the Chemical Potential of a Gas	99
10.5	Other Standard States	100
11	Activities of Nonelectrolytes in Liquid Solutions	103
11.1	General Definition of an Activity	104
11.2	Standard States of Pure Liquid or Solid Compounds	104
11.3	Standard States of Liquids in Mixtures	104
11.4	Standard States in Solutions	105
11.5	Standard State, Activity, and Activity Coefficient of the Solvent	105
11.6	Standard States, Activities, and Activity Coefficients of the Solutes	108
11.6.1	Rational Standard State	108
11.6.2	Practical Standard States	111
11.7	Relations Between Activity Coefficients of the Same Solute, the "Concentrations" of Which Are Expressed According to the Different Scales of Concentrations	113

11.8	Dependence of the Activity Coefficients on Temperature and Pressure	115
11.8.1	With the Temperature	115
11.8.2	With the Pressure	116
12	Activities of Electrolytes	117
12.1	General Considerations	118
12.2	Activity of a Strong Electrolyte	120
12.2.1	Case of the Univalent Electrolytes	120
12.2.2	Case of the Multivalent Electrolytes	121
12.3	Activity of Ions Resulting from the Dissociation of Strong Electrolytes	122
12.3.1	Monovalent Electrolyte MA	123
12.3.2	Multivalent Ions	127
12.3.3	Generalization to Every Strong Electrolyte	129
12.4	Activities of Weak Electrolytes	131
13	Determination of the Activity of the Nonelectrolytes	135
13.1	Activity of One of the Components of a Binary Solution from That of the Other Component	136
13.1.1	Activity of the Solvent from That of the Solute	136
13.1.2	Activity of the Solute as a Function of That of the Solvent	138
13.2	Determination by Measurements of Vapor Pressures	139
13.2.1	Activity of the Solvent a_1	140
13.2.2	Activity of the Solute a_2	140
13.3	Activity of the Solvent from the Determination of Its Freezing Point	142
13.3.1	General Considerations	143
13.3.2	Mathematical Expression Linking the Solvent Activity to the Depression of the Freezing Point	143
13.3.3	Relation Between the Activity of the Solvent and the Temperature of the System	144
13.4	Activity of the Solvent and Osmotic Pressure	147
13.5	Determination of the Activities of Nonelectrolytes by Measurements of the Electromotive Forces	148
13.5.1	General Considerations	148
13.5.2	Example of the Determination of the Activity of Thallium in an Amalgam	149
13.5.3	Determination of the Activity of the Metal in the Amalgam	150
13.5.4	Activity of the Mercury	153
13.6	Determination of the Activities of Nonelectrolytes with Varied Instrumental Methods	153
13.7	Determination of Activities Through Excess Functions and Calculation of Activities Through Empirical Relations	154
13.8	Some Results	155

14	Determination of the Activities of the Electrolytes	157
14.1	Activity of the Electrolytes by the Measurement of the Freezing-Point Depression of the Solvent	158
14.2	Isopiestic Method	160
14.3	Activities from Osmotic Coefficients	162
14.3.1	Rational Osmotic Coefficient	162
14.3.2	On the Physical Significance of the Rational Osmotic Coefficient	163
14.3.3	Practical or Molal Osmotic Coefficient ϕ_m	163
14.3.4	Relation Between Rational and Practical Osmotic Coefficients	164
14.3.5	Theoretical Interest of Handling the Practical Osmotic Coefficient	165
14.3.6	Determination of the Activity Coefficient Starting from the Practical Osmotic Coefficient	166
14.3.7	Practical Interest of the Introduction of Osmotic Coefficients	168
14.4	Determination of the Solute Activity Coefficients from Excess Gibbs Energies	168
14.5	Determination of the Activity Coefficients of the Electrolytes by Measurements of emf	169
14.5.1	Determination with Cells Without Liquid Junction	169
14.5.2	Determination with Cells with Transference	169
14.6	Determination of the Activities of the Electrolytes from Measurements of Their Solubilities	171
15	Debye–Hückel Relations and Neighboring Relations: Calculation of the Activity Coefficient of an Ion	175
15.1	Impossibility of an Experimental Measurement of the Activity of an Ion	176
15.2	Ionic Strength	177
15.3	Influence of the Ionic Strength on the Activity of Nonelectrolytes	178
15.4	General Behavior of the Mean Ionic Activity Coefficients of Electrolytes	179
15.5	Debye–Hückel's Relations	181
15.5.1	The Limit Equation Law	181
15.5.2	Extended Debye–Hückel Relation	182
15.5.3	Other Relations Permitting the Calculation of the Mean Activity Coefficient of an Electrolyte	184

16	Excess Gibbs Energy and Activities	187
16.1	Mixing and Excess Gibbs Energies	188
16.1.1	Mixing Gibbs Energy	188
16.1.2	Ideal Mixing Gibbs Energy	189
16.1.3	Excess Gibbs Energy	189
16.2	Determination of the Activity Coefficients from the Excess Gibbs Energies	190
16.3	A Variant: Simultaneous Obtention of the Practical Osmotic Coefficient and of the Activity Coefficients of the Solutes from the Excess Gibbs Energy	191
16.4	Determination of Activities from Empirical Relations	194
16.5	Calculation of Activities from Excess Gibbs Energy Relations	196
16.5.1	Solutions Without Electrolytes	196
16.5.2	Case of Electrolyte Solutions	198
16.6	Some Methodological Aspects	200
16.7	On the Very Simple Expression (16.11) of an Excess Gibbs Energy	200
16.8	Theoretical Foundation of the Expression of the Excess Gibbs Energy of a Simple Mixture: Meaning of w	202
17	Equilibrium Constant, Activities, and Reaction Gibbs Energy	205
17.1	Reaction Gibbs Energy	206
17.2	Expression of the Reaction Gibbs Energy as a Function of the Activities of the Reactants and Products	207
17.3	Equilibrium Law: Equilibrium Constant	208
17.4	Reaction Standard Gibbs Energy and Reaction Gibbs Energy	209
17.5	Usually Chosen Standard States	212
17.6	Come Back on the Constancy of the Equilibrium Constants	212
17.7	Equilibrium Constant in Homogenous Gaseous Medium	213
17.8	Equilibrium Constants of Reactions in Homogeneous Solutions Resulting from Mixtures from Several Fully Miscible Liquids	214
17.9	Reactions in Dilute Solutions	214
17.10	Heterogeneous Cases	216
17.11	Change in the Equilibrium Constant with Pressure	217
17.12	Change in the Equilibrium Constant with the Temperature	218

18	Obtention of Equilibrium Thermodynamic Constant pH: Definitions and Measurement	221
18.1	Potentiometric Determination of the Mean Activity Coefficient of a Strong Acid	222
18.2	Potentiometric Determination of the Thermodynamic Acidity Constant of a Weak Acid	224
18.3	Potentiometric Determination of the Ionic Product of Water	226
18.4	Conductometric Determination of the Thermodynamic Acidity Constant of a Weak Acid	227
18.5	The Quantity pH	230
18.5.1	Generalities: Formal Definition of pH	230
18.5.2	The Electromotive Force and the Quantity pH	231
18.5.3	Operational Definition of pH	232
19	General Principles of Calculations Involving the Activities of Ionic Species in Solution	237
19.1	Fundamental Difficulty	238
19.2	Nonideality Corrections	238
19.3	Reasoning Allowing the Calculation of the Concentrations of the Different Species at Equilibrium	239
19.4	Taking into Account the Activities	240
19.5	Calculations	241
19.6	Simultaneous Determination of Concentrations, Activities, and Equilibrium Constants Using Computers	243
19.6.1	Determination for a Monoacid	243
19.6.2	Case of the Diacid H_2A	245
19.6.3	Determination of Constants K_{a1} and K_{a2} Without Taking into Account the Activities	245
19.6.4	Taking into Account the Activities	246
 Part II The Activity in Statistical Thermodynamics		
20	Statistical Thermodynamics in Brief	251
21	Concept of Ensembles and Postulates	255
21.1	Strategy: Ensembles and Postulates	256
21.2	Quantum Mechanics: Schrödinger's Equation—Quanto-Energetic States	256
21.3	The Concept of Ensemble of Systems	258
21.4	Postulates	259
22	The Canonical Ensemble: Notion of Distribution	261
22.1	Description of the Canonical Ensemble (N, V, T Imposed)	262
22.2	Strategy	262

22.3	The Mathematical Problem	263
22.3.1	The Notion of Distribution	264
22.3.2	The Notion of Sub-distribution	264
22.3.3	Case of Several Distributions	265
22.4	Obtention of P_j	267
22.4.1	Great Number of Distributions: Method of the Maximal Term	267
22.4.2	Calculations	268
23	Thermodynamic Quantities Within the Framework of the Canonical Ensemble	271
23.1	Association Average Energy \bar{E} and Internal Energy	272
23.2	Statistical Expression of the Entropy	273
23.3	The Characteristic Function of the Canonical Ensemble	275
23.4	Calculation of the Thermodynamic Functions by Starting from the Characteristic Function of the Canonical Ensemble	276
23.4.1	The Entropy	277
23.4.2	The Pressure	277
23.4.3	The Internal Energy	277
23.4.4	The Chemical Potential	277
23.5	Degenerated Energy States E_j and Energy Levels	278
24	Other Ensembles	279
24.1	Grand Canonical Ensemble or Grand Ensemble	279
24.1.1	Generalities	279
24.1.2	Grand Ensemble and Absolute Activity	285
24.1.3	The Case of Several Components (Grand Ensemble)	286
24.2	Microcanonical Ensemble: Boltzmann's relation	287
24.3	Isothermal-Isobaric Ensemble	289
25	Systems of Molecules or Subsystems: Independent, Distinguishable, and "Indistinguishable"	291
25.1	Meaning of the Independence of the Molecules and "Subsystems"	291
25.2	Calculation of the Partition Function of Independent and Distinguishable Molecules or Subsystems	292
25.2.1	Definition of the System	292
25.2.2	Calculation of the Partition Function	293
25.3	Independent and "Indistinguishable" Molecules or Subsystems	293
26	Perfect Gases	295
26.1	Definitions	296
26.2	A Brief Discussion of These Definitions	296

26.3	Types of Perfect Gases: The Case of Mixtures	297
26.4	The State Equation in Statistical Thermodynamics	297
26.5	Obtaining the Perfect Gas Law Using an Ensemble of Identical Molecules Without Mutual Interactions and Being “Indistinguishable”	297
26.6	A Study of Perfect Monoatomic Gases	299
26.6.1	Translation Energy and Internal Energy	299
26.6.2	Expression of the Molecular Partition Function of Translation q^{tr}	300
26.6.3	de Broglie’s Thermal Wavelength	301
26.6.4	Expression of $\ln Q$ as a Function of the Atomic Parameters	301
26.6.5	Helmholtz Energy A	301
26.6.6	Pressure	302
26.6.7	Internal Energy E	302
26.6.8	Entropy	303
26.6.9	Gibbs Energy G	303
26.6.10	Chemical Potential μ	304
26.6.11	Standard Chemical Potential of a Perfect Gas	304
26.7	Binary Mixture of Two Perfect Monoatomic Gases	305
26.8	The Perfect Gas Law from Other Ensembles	306
26.9	Perfect Polyatomic Gases	306
27	Classical Statistical Mechanics, Configuration, and Classical Canonical Partition Function	309
27.1	Classical and Quantum Mechanics	310
27.2	Quantum and Classical Mechanics in Statistical Thermodynamics	310
27.3	Cartesian Coordinates of a Specific Particle in a System	311
27.4	Configuration of a System	311
27.5	Spherical Coordinates ϕ, θ, r of a Particle	312
27.6	Classical Analogue of the Quantum-Mechanical Canonical Partition Function	313
27.7	Condition Required for the Applicability of the Partition Functions (27.1) and (27.3)	315
27.8	Some Examples of Handling of Classical Partition Functions: The Case of Perfect Gases	316
28	The Configurational Partition Function: Molecular Distribution Functions	319
28.1	The Configuration Integral Z_N	320
28.2	Basic Distribution Function	322
28.3	Average of Any Quantity $F(\mathbf{R}^N)$	322
28.4	Molecular Distribution Functions	323
28.4.1	Specific Distribution Functions	324

28.4.2	Generic Distribution Functions	324
28.4.3	Examples	324
28.5	Pair Correlation Function and Radial Distribution Function	326
29	Radial Distribution Function	329
29.1	Definition of the Radial Distribution Function	330
29.2	Physical Meaning of the Radial Distribution Function	331
29.3	Another Expression of the Radial Distribution Function	331
29.4	The Curve $g(R)/R$	332
29.5	Radial Distribution Functions of Some Systems	333
29.5.1	Perfect Gas	333
29.5.2	Radial Distribution Function of a Gas with a Low Density Number	334
29.6	Determination of the Radial Distribution Function	335
30	Radial Distribution Function and Thermodynamic Quantities: Calculation of the Internal Energy and of the Pressure of the System	337
30.1	The “Pairwise Additivity” Hypothesis	338
30.2	Gaining the Relations Being Searched for: Principle	338
30.3	Radial Distribution Function and Internal Energy of a System	341
30.4	Radial Distribution Function and Pressure of the System. Equation of State of a Perfect Gas	342
31	The Radial Distribution Function and the Isothermal Compressibility Coefficient of a System	345
31.1	The Generic Molecular Distribution Function in the Grand Ensemble	346
31.2	Radial Distribution Function and Isothermal Compressibility Coefficient of the System	348
32	The Chemical Potential and the Radial Distribution Function: General Formal Introduction of the Activity and of the Activity Coefficient	353
32.1	General Relations	354
32.2	The Case of a Perfect Gas	355
32.3	A General Formal Expression of the Chemical Potential When There Exist Interactions Between the Particles of the System	356
32.4	A General Expression of the Chemical Potential in the Framework of the “Pairwise Additivity” Hypothesis	358
32.5	A General Meaning of the Activity Coefficient	360

32.6	The Chemical Potential and the Radial Distribution Function	361
32.7	Relation Between the Chemical Potential and the Function G	362
33	Virial Coefficients in Terms of Interaction Potential Energies:	
	Mayer's Theory	365
33.1	Difference Between Perfect and Imperfect Gases	366
33.2	The Virial Expansion	366
33.3	Virial Coefficients and Parameters Coming from Statistical Thermodynamics	367
33.3.1	Setting Up the Relation Between λ and \bar{p}	368
33.3.2	Expressions of the Virial Parameters $B_n(T)$ Containing the Canonical Partition Functions	370
33.4	Physical Significance of the Virial Coefficients of a Monoatomic Gas in Statistical Mechanics	371
34	A Statistical Expression of the Activity of a Species:	
	A Relation Between It and the Corresponding Concentration in the Case of an Imperfect Gas	375
34.1	The Followed Reasoning	376
34.2	Introduction of the Activity	377
34.3	Analogy of the Behaviors of z and of ρ When ρ Tends Toward Zero	378
34.4	Relation Between the Number of Density ρ and Activity z . . .	379
34.5	Discussion Around the Relation Between the Activity and the Corresponding Concentration of the Imperfect Gas	383
34.6	Relations Between the Density Number of the Gas, Its Activity, and the Virial Coefficients	383
34.7	Justification of the Preceding Calculations. Validity of the Statistical Definition of the Activity	384
34.8	Identity of Z'_N and of the Integral of Configuration in Classical Statistical Thermodynamics Z_N	386
34.9	Physical Meaning of the Activity of a Gas	387
34.10	Definition of the Fugacity	388
34.11	Virial Coefficients and Configuration Integrals	388
35	Activities of Gases in a Mixture of Imperfect Gases	391
35.1	Activity of Both Gases	391
35.2	Chemical Potentials of Both Components as a Function of Their Partial Pressure	395
36	Chemical Equilibrium Between Gases and Statistical Thermodynamics	399
36.1	Some Recalls: Chemical Equilibria and Classical Thermodynamics	400

36.2	Equilibrium Constants and Molecular Partition Functions of the Reactants and Products: Case of a Mixture of Ideal Gases	400
36.3	A Simple Example: A Dimerization Equilibrium	402
36.4	Chemical Equilibrium Between Imperfect Gases	404
37	Activity Coefficients of Gases	407
37.1	The Activity Coefficient at the Molecular Level	407
37.2	Expression of the Activity Coefficient of a Real Gas	409
38	Activities and Concentrations of Nonelectrolytes in Dilute Liquid Solutions Study of the Osmotic Pressure	413
38.1	The Main Difference Between the Cases of a Mixture of Real Gases and of Solutions	414
38.2	Osmotic Equilibrium	414
38.3	Some Results Stemming from the McMillan–Mayer’s Theory	414
38.4	Fundamental Aspects of the McMillan–Mayer’s	415
38.5	Some Features of the McMillan–Mayer’ Theory	416
38.6	Obtaining the Relations (38.1) and (38.2)	420
39	Relation(s) Activity: Concentration of Nonelectrolytes in Dilute Liquid Solutions at Constant Pressure and Temperature	423
39.1	The Studied Physical Process	424
39.2	Study	424
39.2.1	Formalism	424
39.2.2	Definition of the Activity	425
39.2.3	Calculations	426
39.3	Relation Being Searched for	429
40	Activity Coefficient of a Solute	431
40.1	Expression of the Activity Coefficient of the Solute in Terms of Experimental Parameters When an Osmotic Pressure is Developing	432
40.2	A New Type of Activity Coefficient Applying to the Osmotic Equilibrium	434
40.3	Activity Coefficient in the Case of a Binary Mixture at Constant Temperature and Pressure	436
41	Molecular Distribution Functions in Binary Mixtures	439
41.1	The Notion of “Pairwise Additivity” in the Case of Mixtures	439
41.2	Density of Base Probability in the Canonical System	440
41.3	Molecular Distribution Functions	441

42	Kirkwood–Buff’s Theory: Changes of Solutes Chemical Potentials with the Concentrations at Constant Pressure and Temperature	443
42.1	An Overview of Kirkwood–Buff’s Theory	444
42.2	Kirkwood–Buff Integrals $G_{\alpha\beta}$	444
42.3	Different Steps of the Setting-Up of the Kirkwood–Buff’s Theory	445
42.4	First Step: Expressions Relating Functions $G_{\alpha\beta}$ to the Average Density Numbers of the Components	445
42.5	Second Step: Mathematical Relations Between Some Partial Derivatives Involving the Chemical Potentials of the Different Components	446
42.6	Third Step: Expressions of Thermodynamic Quantities as Functions of Kirkwood–Buff Integrals	448
42.7	Some Important Relations Stemming from the Kirkwood–Buff’s Theory	448
42.8	Expression of the Derivative of the Chemical Potential of a Component with Respect to Its Molar Fraction at Constant Molar Concentration of the Other	449
42.9	Some Aspects of Kirkwood–Buff’s Theory	450
43	Chemical Potentials of the Components of Ideal Solutions of Nonelectrolytes	453
43.1	Looking Back on the Definition of Ideal Solutions	454
43.2	Perfect Solutions: Mixtures of Two Very Similar Components	454
43.3	Ideal Solutions: Very Dilute Solutions	457
44	Chemical Potentials of Components of Binary Nonideal Solutions of Nonelectrolytes	461
44.1	Derivatives of the Chemical Potentials of a Solution Components with Respect to Their Molar Fractions	462
44.2	Chemical Potentials of the Components of a Solution, the Behavior of Which Weakly Deviates from that of a Perfect Solution	462
44.3	Chemical Potentials of Components of Nonideal, Insufficiently Dilute, Solutions	463
44.3.1	Chemical Potentials in Nonideal, Dilute Solutions on the Density Numbers Scale	463
44.3.2	Some Supplementary Considerations Concerning the Chemical Potential of the Solute at Constant Temperature and Pressure: The Part Played by the Scale of Concentrations	465
44.3.3	Solvent Chemical Potential	467

45	Expressions of Activity Coefficients and Activities in Relation to Kirkwood–Buff’s Theory	469
45.1	Some Introductory Points: Different Kinds of Ideal Solutions	470
45.2	Expressions of the Activities and of the Activity Coefficients in the Case of Symmetric Nonideal Solutions . . .	471
45.3	Expressions of Activity Coefficients and Activities of the Components of Nonideal Dilute Solutions	474
45.4	Multiplicity of Activities: Other Kinds of Activities	477
45.5	Meaning of the Parameter Δ_{AB}	478
46	Debye–Hückel Theory	479
46.1	Intermolecular Forces	480
46.2	Strategy Followed in the Drawing Up of the Debye–Hückel Theory	481
46.3	Hypotheses on Which Is Based the Debye–Hückel Theory . . .	484
46.4	Schematic Representation of the Solution of an Electrolyte . . .	485
46.5	The Basic Equation of the Debye–Hückel Theory: The Poisson–Boltzmann Equation	486
46.6	On the Legitimacy of the Poisson–Boltzmann Equation	488
46.7	A Solution of the Poisson–Boltzmann Equation and Some Inferences	488
46.8	Limiting Equation of Debye–Hückel	491
46.8.1	Calculation of the Corrective Term of the Gibbs Energy of Ions–Ions Interactions	491
46.8.2	Expression of the Activity Coefficient γ_{\pm} of One Ion	492
46.8.3	Introduction of the Ionic Strength	492
46.8.4	The Limit Debye–Hückel Equation	493
46.9	On the Agreement of the Limit Equation with Experiments	494
46.9.1	Relation Derivating from the Limit Equation the Results of Which Can Be Directly Confronted with the Experimental Results	494
46.9.2	Agreement of the Debye–Hückel Limiting Law with Experiments	495
46.10	Limitations of Debye–Hückel Limiting Equation	497
46.11	Possible Causes of the Limitations of the Debye–Hückel Limiting Equation	498
46.12	Ions Have a Finite Size Radius: The Extended Debye–Hückel Theory	500
46.13	On the Meaning of the “Ion Size Parameter”	500
46.14	Other Causes of Discrepancy Between the Experiments and the Debye–Hückel Laws	502
46.14.1	Solvation of the Ions of the Electrolyte	502

46.14.2	The Adoption of the Boltzmann's Definition for the Density ρ_r	503
46.14.3	Change of the Dielectric Constant with the Ions Concentrations in the Solution	503
46.14.4	Formation of Ion-Pairs and of Superior Aggregates	504
46.14.5	Legitimacy of the Series Development of the Boltzmann's exponential	505
47	Radial Distribution Functions and Electrolytes Solutions Theory	507
47.1	Informatic Simulation Techniques	507
47.1.1	Generalities	508
47.1.2	The "Monte Carlo" Approach	509
47.1.3	Molecular Dynamic Technique	509
47.1.4	Some Remarks	510
47.2	General Principle of the Calculation of the Activity Coefficients of the Electrolytes Through the Use of the Kirkwood–Buff Theory	511
47.3	Radial Distribution Functions and the Corresponding Theory of the Electrolytes	511
47.3.1	Radial Distribution Functions Only Involving Interactions Between Two Species	511
47.3.2	Radial Distribution Functions More Complex	512
47.4	Debye–Hückel Theory and Radial Distribution Function	513
47.4.1	The Radial Distribution Function in the Debye–Hückel Theory	513
47.4.2	Some Advantages of the Approach Through the Radial Distribution Functions	513
47.5	Some Results	514
48	The Activity Concept in Retrospect	517
48.1	Lewis' General Definition of Activity	517
48.2	Interesting Features of the Introduction of Activities	518
48.3	Ideal Solutions: Causes of Deviation from the Ideal Case	519
48.4	The Activity Coefficient	520
48.5	Multiplicity of the Activities of a Species in a Given Thermodynamic State	520
48.6	On the Arbitrary Character of the Definition of an Activity: The Standard State	520
48.7	Standard States Usually Chosen	521
48.8	Activities, Equilibrium Constants, and Gibbs Energy Changes Accompanying Processes	522
48.9	Other Definition of the Activity of a Species	522

48.10	Activity Coefficients, Activities, and Deviations from the Ideal Behavior in the Case of a Liquid or a Solution	523
48.11	Activities of Nonelectrolytes and Molecular Quantities	523
48.12	Activities of Electrolytes: Expressions of Activities and of Activity Coefficients of Electrolytes in Terms of Molecular Parameters	526
48.13	Determination of Activities	529
Appendix A: Mathematical Apparatus		531
Appendix B: Relation Between the Activity $a_{C\ i}$ and the Fugacity of a Gas (viz. Chap. 10)		537
Appendix C: Integration of the Equation $d\ln a_{\pm} = d\theta/\nu\lambda m + \alpha\theta d\theta/\nu m$		539
Appendix D: Determination with Cells with Transference		541
Appendix E: Kielland's Tables		545
Appendix F: Classic Canonical Partition Function		549
Appendix G: The Concept of Fugacity		557
Appendix H: Ideal Solutions		559
Appendix I: Definitions of Activity		563
Appendix J: Activity of a Gas		565
Appendix K: Activities of Nonelectrolytes in Solutions		567
Appendix L: Partition Functions in the McMillan–Mayer's Theory		571
Appendix M: Relations Between π and the Virial Coefficients and Also with the Density Number ρ_2 (First Step)		575
Appendix N: Relations Between π and the Virial Coefficients and Also with the Density Number ρ_2 (Second Step)		577
Appendix O: Meaning of the Ratio $\Delta_N\Delta_0^{N-1}/\Delta_1^N$		581
Appendix P: Work and Electrostatic Interactions Energy		583

Appendix Q: Poisson's Relation	587
Appendix R: Change of Coordinates in Poisson's Equation	591
Appendix S: General Principles of Calculations of Ionic Species Concentrations in Solutions Involving Activities	593
Appendix T: Solution of Poisson–Boltzmann's Equation and Inferences	595
Appendix U: Extended Debye–Huckel Equation	599
Appendix V: Demonstration That the Function PV Is the Function: Characteristic of the Grand Canonical Ensemble	603
Bibliography	607

The Notion of Activity in Chemistry

Burgot, J.-L.

2017, XLI, 608 p. 51 illus., Hardcover

ISBN: 978-3-319-46399-5